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16. ABSTRACT

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SORPTION OF HYDROPHOBIC POLLUTANTS ON NATURAL SEDIMENTS

SAMUEL W. KARICKHOFF, DAVID S. BROWN and TRUDY A. SCOTT

Environmental Research Laboratory, U.S. Environmental Protection Agency, College Station Road, Athens, GA 30605, U.S.A.

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Abstract—The sorption of hydrophobic compounds (aromatic hydrocarbons and chlorinated hydrocarbons) spanning a concentration range in water solubility from 500 parts per trillion (ppt) to 1800 parts per million (ppm) on local (North Georgia) pond and river sediments was investigated. The sorption isotherms were linear over a broad range of aqueous phase pollutant concentrations. The linear partition coefficients (K_p) were relatively independent of sediment concentrations and ionic strength in the suspensions. The K_p's were directly related to organic carbon content for given particle size isolates in the different sediments. On an organic carbon basis ($K_{oc} = K_p$/fraction organic carbon), the sand fraction (>50 μm particle size) was a considerably less effective sorbent (50–90% reduction in K_{oc}) than the fines fraction (<50 μm particles). Differences in sorption within the silt and clay fractions were largely related to differences in organic carbon content. Reasonable estimates of K_{oc}'s can be made from octanol/water distribution coefficients, which are widely catalogued or easily measured in the laboratory.

INTRODUCTION

The fate of hydrophobic organic pollutants (compounds having a water solubility of less than a few parts per million) in a natural water system is highly dependent upon their sorptive behavior. In addition to affecting the physical movement of pollutants, sorption can be involved directly in pollutant degradation via surface-associated chemical processes. Moreover, natural sediments can indirectly mediate solution-phase processes by altering the pollutant concentration in solution or by providing a buffered solution-phase ion suite that may affect the dielectric properties and acidity of the solution phase. A realistic key to predicting the environmental fate of hydrophobic compounds then, lies in an understanding of sediment-related processes.

Existing data point to a large number of different sorbent properties as keys to sorption in given situations (Hamaker, 1975; Pionke & Chesters, 1973; Bailey & White, 1970). The high degree of variability and complexity in sediment composition and potential sorptive interactions seems to preclude the possibility of developing a simple, systematic procedure for predicting sorption parameters. A general predictor, on the other hand, that would take into account detailed sorbent structure and associated physical properties would be useless for most applications because of its complexity. Acceptability of a predictor depends upon the use to be made of the resulting number(s), the span of environmental conditions over which the predictor is to be applied, and the degree of accuracy or precision required in its usage. The primary goal is to define a limited set of sorbent properties that can generate a sorption predictor (generally within a factor of 2) over a broad range of environmental conditions in sediment–water systems.

Significant contributions to the systematization and estimation of sorption in natural systems are the works of Lambert (1966, 1978, 1968) and co-workers (Lambert *et al.*, 1965). Lambert has demonstrated that for a given soil type, the sorption of neutral organic pesticides can be well correlated with the organic matter content of the soil. His approach corrects for sorptive differences in different soil types by defining an 'effective organic matter', which is derived for a given soil by normalizing soil sorption of a known compound to a reference or standard soil system. Lambert and others (Briggs, 1969; Hance, 1969) have utilized an extrathermodynamically based framework, similar to that used by Bark & Graham (1966) for chromatographic sorbents, to compute sorption constants. Lambert further suggested that the role of soil organic matter was similar to that of an organic solvent in solvent extraction and that the partitioning of a neutral organic compound between soil organic matter and water should correlate well with its partitioning between water and an immiscible organic solvent. Briggs (1973) developed a regression equation relating the soil sorption of phenyl urea herbicides to their octanol–water partitioning.

The work of Lambert and Briggs was done in pesticide-soil systems as was the overwhelming majority of sorption work in systems of environmental interest. The interrelationship of the sorption behavior of soils and sediment is largely unknown. Poinke & Chesters

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Table 1. Materials used in study

Material	Description
Sediments	
Doe Run	Small pond sediment—grass watershed Sand (50%)*, silt (50%), clay (1%)
Hickory Hill	Small pond sediment—wooded watershed sand (50%), silt (50%), clay (1%)
Oconee River	Small river—sand (90%), silt (5%), clay (5%)
Class 1 hydrophobic compounds	
Pyrene	K & K Labs; recrystallized from ethanol
Methoxychlor	EPA, Research Triangle Park, NC; Standard—used as received
Tetracene	Analabs, Inc.; used as received
Anthracene	Analabs, Inc.; used as received
9-Methylanthracene	K & K Labs.; recrystallized from ethanol
Phenanthrene	K & K Labs.; recrystallized from ethanol
2,4,6,2',4',6'-Hexachlorobiphenyl	RFR Corp.; used as received
Class 2 hydrophobic compounds	
Naphthalene	Baker; extracted with, and recrystallized in, hot water
2-Methylnaphthalene	Eastman; extracted with, and recrystallized in, hot water
Benzene	Fisher; spectrograde, used as received

* Approximate particle size distribution in parentheses.

(1973) have reviewed interactions of pesticides with sediment–water systems and have outlined compositional distinctions between soils and sediments that can affect sorption. A key distinction between the two systems is particle size composition and its potential impact upon environmental behavior. Sediments are largely eroded soils that have been subjected to continuous redispersion and particle-size fractionation commencing with runoff and continuing with subsequent water-system processes. These processes are highly dependent upon the dynamics of the specific stream, river, pond, or lake and upon the dispersion properties of the parent soil. One result is that sediment within a given water compartment may contain a very narrow range of particle sizes. For example, a suspended sediment within a river system may be largely clay, a bottom sediment from the middle of the river largely sand, and a bottom sediment from the edge largely silt. Functional dependence on particle size could vary the degree of sorption in different river compartments or produce a nonuniform distribution of sorbed pollutant within the sediment. Richardson & Epstein (1971) showed that two hydrophobic compounds, DDT and methoxychlor, tend to concentrate in finer particle sizes (clay), whereas the more soluble endosulfan preferred coarser material.

The work reported investigated the sorption of polycyclic aromatics and chlorinated hydrocarbons, two hydrophobic organic families, on river and pond sediments. Special emphasis was placed on the sorption role of sediment particle size and organic matter content and upon the correlation of sorption with sorbate aqueous solubility and octanol/water distribution coefficients.

MATERIALS AND METHODS

Sediment preparation

The three bottom sediments (Table 1) collected for study provide a range of water sources and associated compositional differences; no effort was made to collect samples that would characterize a given source or geographical region. Particle size fractionation procedures were similar to those of Jackson (1956) except that no dispersants or other additives were used. The sand and silt fractions were separated by sedimentation and the clay retained in the suspended form. The sand and silt fractions were washed 5 times with the first two washes being retained for further separation. The particle size separates were: sand (>50 m), coarse silt (50–20 μm), medium silt (20–5 μm), fine silt (5–2 μm), and clay (>2 μm). Galbraith Laboratories, Inc., Knoxville, TN, performed the organic carbon analyses. Organic carbon was determined as total carbon (Leco dry combustion) minus inorganic carbonates (gas purge of acidified suspensions).

Sorption isotherms

Adsorption isotherms for a series of hydrophobic compounds (Table 1) were run by a variety of methods dependent upon the water solubility and volatility from sediment suspensions of the materials.

All isotherm determinations involved the equilibration at 25°C (±1°C) of variable concentrations of compound with constant concentrations of sediment. The sorbent concentrations (air-dry mass basis) generally used were 400 mg ml^{-1} of suspension for sand, 20 mg ml^{-1} for coarse and medium silt, 10 mg ml^{-1} for fine silt and 1 mg ml^{-1} for clay. These concentrations varied somewhat depending upon the amount of sediment fraction available.

The amounts of a given compound added to the sediment samples were chosen to give, on the high and low concentration ends of the isotherm, solution concentrations approximately 50 and 10%, respectively, of the compound water solubility. Each isotherm involved at least 12 interim points, and all isotherms were replicated at least once. Compounds were handled so as to minimize

exposure to laboratory lighting except in cases where light stability was checked. The mixing of the compounds and sediments proceeded in one of two ways:

1. Class 1 compounds (low volatility materials having water solubility of <500 ppb). These low-water-solubility compounds are difficult to store and transfer in aqueous solutions. Also, the major portion of these compounds tended to sorb when an aqueous solution of the compound was mixed with sediment, which prevented the achievement of the desired isotherm span. To circumvent these problems, the compounds were 'plated' out of hexane or isooctane solutions onto Erlenmeyer flasks. Sediment suspensions were added, and the containers swirled on an oscillating shaker until equilibrium was achieved. Equilibration, as judged by sequential sampling, was generally achieved within 24 h. Unless the compound started to show losses (e.g. 3-ring polycyclics), however, the suspensions were allowed to mix for 48 h.

2. Class 2 compounds (volatile materials having a water solubility of ≥ 500 ppb). Aliquots of aqueous stock solutions of the hydrophobic compounds were mixed with sediment suspensions in stainless steel centrifuge tubes fitted with a sealable cap. Compound attenuation prohibited the attainment of a stable equilibrium such as was achieved for the previous group of compounds; 4–8 h of shaking was generally sufficient to produce a fairly constant (variation $<10\%$) partition response, yet not result in compound attenuation in excess of 10% of the total present.

Subsequent to compound–sediment equilibration, the suspensions were centrifuged at 20,000 rev min^{-1} (Sorvall RC2-B with SS-34 rotor) for 60 min. Analyses were run on water phase aliquots taken from the upper portion of the centrifuge tube; sorbed compound concentrations were computed by difference based on the total compound added. Mass balance was checked on about half of the samples by soxhlet extraction of the sediment phase with hexane. Recoveries were in excess of 90% for all compounds.

Analyses for polycyclic hydrocarbons were conducted by u.v. light absorption on a Perkin–Elmer 356 spectrophotometer; chlorinated hydrocarbon analyses were performed on a Tracor 222 gas chromatograph equipped with a Ni^{63} electron capture detector and a 3% SE-30 Gas Chrom Q Column.

Partitioning as measured via sediment–water phase separation effected by filtering the suspensions through Zitex membranes (75-F, 2–5 μm pore size, Chemplast, Inc., Wayne, NJ) was compared with centrifugation results for both pyrene and methoxychlor for Doe Run medium and coarse silt. Consecutive aliquots of the filtrate were analyzed until a constant response was obtained indicative that the test compound was not being further removed by the filter material.

Desorption isotherms for pyrene and methoxychlor were run on the Doe Run coarse silt. Sediment that had been equilibrated with the compounds was removed by sedimentation and centrifugation (to remove any unsettled particles). The compound-spiked sediment was resuspended and allowed to equilibrate under swirling for 24 h and partitioning was determined as in previous adsorption runs.

The dependence of adsorption isotherms on sediment concentration and salt content was determined for pyrene on the Doe Run medium silt. Silt concentrations were varied from 2 to 20 mg ml^{-1} in 2 mg ml^{-1} increments while keeping the pyrene concentration relative to dry mass sediment constant. In the salt-spiked isotherms, a series of isotherms were run wherein the NaCl additions to the suspensions were varied from 0 to 20 mg ml^{-1} of suspension in increments of 2 mg ml^{-1}.

Octanol water partitioning

Reagent grade octanol was extracted once with 0.1 N NaOH, twice with distilled water, and was subsequently distilled twice. The compounds were prepared in octanol at or near saturation concentrations for the solids or approximately 0.1% for liquids. A small volume of this octanol solution (1–5 ml) was equilibrated with variable volumes of water (determined by the amount of compound required for analysis and thus the analytical sensitivity and water solubility of the compound). After equilibration, the phases were separated and each phase analyzed for the designated compound. For many compounds (especially Class 1 compounds), a crystalline third phase appeared upon mixing the spiked octanol with water; in the presence of the crystalline phase, the aqueous phase concentrations were generally within experimental error of the distilled water solubilities. Phase separation for nonvolatile (class 1) compounds involved standing plus centrifugation to further resolve the phases. The volatile compounds (class 2) were equilibrated in sealed centrifuge tubes, centrifuged, and the liquid phases sampled out of the tubes. In all cases, the octanol-phase samples were diluted with hexane or isooctane for analysis; the water phase samples were extracted with hexane.

Additional distribution ratios were determined at reduced concentrations (i.e. water concentrations $\leq$ half the water solubility) by dilution of the stock octanol solutions prior to mixing with water. The presence of interfering, more-water-soluble-impurities was checked by sequentially equilibrating the spiked octanol with aliquots of water, and establishing the constancy of the partitioning ratio. All determinations were in quadruplicate, with at least eight total determinations per compound.

RESULTS AND DISCUSSION

Sorption isotherms on particle size isolates

In-depth studies of the dependence of sorption on sediment particle size and organic matter content were carried out on pyrene and methoxychlor. Representative adsorption isotherms on the particle size isolates are shown in Figs. 1 and 2. General features concerning the isotherms include:

1. The adsorption data for all systems fitted well to linear isotherms over a broad range of water phase concentrations. That is,

$$X = K_p C \tag{1}$$

where X denotes the concentration of sorbate on the sediment, relative to dry weight (for these compounds, conveniently expressed as ppb); C is the equilibrium solution sorbate concentration (ppb) and K_p is the partition coefficient. Deviations from linearity (least-squares fitted) approximated deviations in replicate determinations for individual isotherm points. As the sorbate water concentration approached 60–70% of the sorbate aqueous solubility, the isotherms typically bent upward, indicative of increased sorption. Because no distinction was made between sorbed and crystalline sorbate, however, these deviations from isotherm linearity may reflect the presence of a crystalline phase rather than increased sorption. Our study focused on the linear portion of the isotherms, which has more widespread environmental significance.

2. The sorption appeared reversible in all systems. Linear-least-squares fitting of the 'linear' portions of the isotherms gave ordinate intercepts that were small

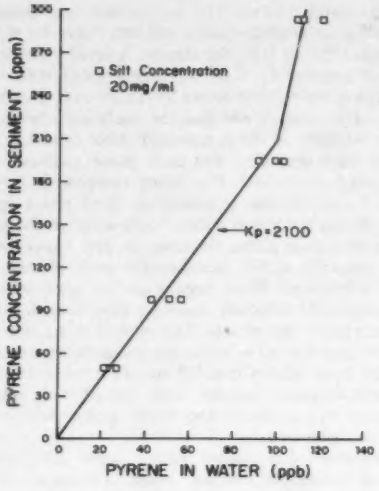

Fig. 1. Adsorption isotherm for pyrene on the Doe Run coarse silt.

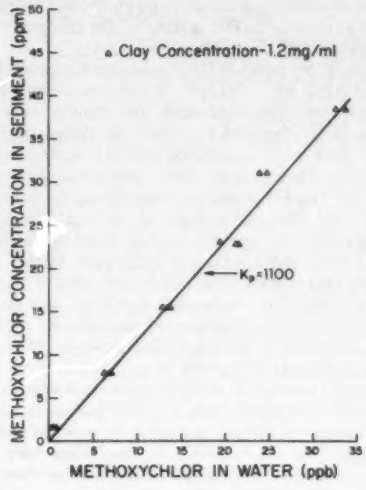

Fig. 2. Adsorption isotherm for methoxychlor on Hickory Hill clay.

(e.g. intercept was less than 20% of the lowest measured sorbed concentrations). In general there were as many negative-valued intercepts as positive. The average intercept value was near zero over all systems.

Desorption isotherms for both the pyrene and methoxychlor runs on the Doe Run coarse silt were within experimental error of the respective adsorption isotherms; no hysteretic effects were observed.

3. Filtering and centrifugation gave comparable isotherms. Isotherms determined on the Doe Run medium and coarse silts (pyrene and methoxychlor) by filtering the suspensions through halocarbon membranes were within experimental error of those determined by centrifugation.

4. The linear portion of the isotherms was independent of sediment concentration in dilute suspensions. Varying the Doe Run medium silt concentration from 2 to 20 mg ml^{-1} (2 mg ml^{-1} increments), while keeping the total pyrene concentration relative to dry silt mass constant at 30 ppm, produced no real (i.e. beyond experimental error) change in the aqueous phase concentration of pyrene (10 ± 2 ppb). When the total pyrene relative to sediment was increased to 150 ppm (near the limit of linear isotherm behavior), however, the same increase in sediment concentration produced a gradual decrease in aqueous-phase pyrene concentration from 50 ± 2 to 40 ± 5 ppb.

5. The isotherms showed only a slight dependence on ionic strength. The incremental addition of NaCl (0–20 mg ml^{-1} in 2 mg ml^{-1} increments) to a Doe Run medium silt—pyrene suspension resulted in an approximately linear increase in K_p. A salt content equal in mass to the sediment content (20 mg ml^{-1}) produced approximately a 15% increase in K_p over the 'no salt' system.

6. Sorbates in a mixture sorbed independently. The sorption isotherms of pyrene and phenanthrene were determined in combination and individually on both the Doe Run and Hickory Hill coarse silts. Only the linear portion of each isotherm was followed, but the combined isotherms showed no discernible sorptive interaction between these two sorbates.

Sorption dependence on sorbent properties

Table 2 shows the partition coefficients for pyrene and methoxychlor on the various particle size isolates. Organic matter content and sediment particle size were the two sorbent properties investigated. Pyrene and methoxychlor showed very similar sorptive dependencies on these sorbent properties. Figures 3 and 4 show the individual K_p's plotted as a function of organic carbon content. Two features of sorptive behavior are apparent in these figures. First, the K_p's of both pyrene and methoxychlor show, in general, a linear increase with organic carbon content. Least squares correlation coefficients (γ_{xy})* are indicated in the figures. Second, the functional behavior of the sand fraction can be distinguished from that of the finer (< 50 μm) sediments. When sorption is 'keyed' solely to organic carbon, it is convenient to define

$$K_{oc} = K_p/oc, \qquad (2)$$

where oc is the fractional mass of organic carbon in the sediment. Table 3 gives the mean K_{oc}'s for pyrene and methoxychlor and variations over the sediments studied. A bell-shaped dependence of K_{oc} on particle size is apparent, starting with a low K_{oc} value for

* It should be emphasized that this empirical relationship does not determine that hydrophobic organic compounds are sorbed to organic components of the sediment, although this may in fact be the case. Instead, both sorption and organic carbon content may be directly related to another sediment property (or properties).

Table 2. Pyrene and methoxychlor sorption coefficients for linear portion of isotherms

Sediment size fraction	organic carbon	Pyrene K_p	(r^2)	Pyrene K_{oc} ($\times 10^{-5}$)	Methoxychlor K_p	(r^2)	Methoxychlor K_{oc} ($\times 10^{-5}$)
Hickory Hill							
Sand	0.13	42	(0.85)	0.32	53	(0.85)	0.41
Coarse silt	3.27	3000	(0.95)	0.92	2600	(0.97)	0.80
Medium silt	1.98	2500	(0.95)	1.3	1800	(0.91)	0.91
Fine silt	1.34	1500	(0.90)	1.1	1400	(0.97)	1.0
Clay	1.20	1400	(0.75)	1.2	1100	(0.99)	0.92
Doe Run							
Sand	0.086	9.4	(0.97)	0.11	8.3	(0.98)	0.097
Coarse silt	2.78	2100	(0.92)	0.76	2200	(0.93)	0.80
Medium silt	2.34	3000	(0.80)	1.3	1700	(0.94)	0.73
Fine silt	2.89	3600	(0.88)	1.2	2300	(0.95)	0.80
Clay	3.29	3800	(0.90)	1.2	2400	(0.98)	0.73
Oconee River							
Sand	0.57	68	(0.38)	0.12	95	(0.93)	0.17
Coarse silt	2.92	3200	(0.99)	1.1	2500	(0.97)	0.86
Medium silt	1.99	2300	(0.96)	1.2	2000	(0.93)	1.0
Fine silt	2.26	2500	(0.99)	1.1	2100	(0.96)	0.93
Clay*							

* The clay portion of this sediment was allowed to age in suspension and degraded substantially. Therefore, no sorption was done on this fraction.

the sand, increasing to a maximum in the medium or fine silt, then decreasing somewhat for clay-sized particles. For a whole sediment, the observed K_p is given by

$$K_p = \Sigma_i K_p^i f_i, \tag{3}$$

where i denotes the (i)th size fraction, and f_i is the fraction of the total mass represented by component i. By using organic carbon as the sole sorbent property required to determine K_p^i.

$$K_p = \Sigma_i K_{oc}^i f_i (oc)_i. \tag{4}$$

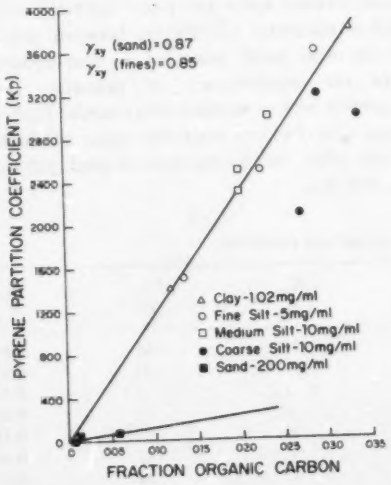

Fig. 3. Pyrene K_p as a function of sediment organic carbon.

Therefore, given the set of 'sediment-independent' K_{oc}^i, organic contents, and fractional masses of the size fraction, one can compute the composite K_p for any given sediment†. The K_{oc}^i could be determined by sorption measurements on particle-size isolates of any given sediment, but a simpler and more easily performed procedure was desirable.

For purposes of K_p estimation, the fines are not subdivided; the range in the variation of K_{oc} within the fines is acceptable, and most likely within the limits of accuracy available for definition of particle size distribution and/or organic carbon contents. For both methoxychlor and pyrene, the K_p's for sand were 0.5–4% of those for the next finer fraction. This was largely caused by the low organic carbon contents

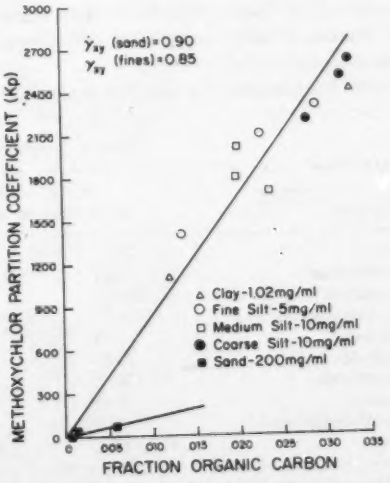

Fig. 4. Methoxychlor K_p as a function of sediment organic carbon.

† To date, only local sediments have been investigated: sediment collection is underway to extend this study to a national sediment basis.

Table 3. Average K_{oc} values on all sediments

Sediment	Pyrene	Methoxychlor
Sand	19,000 (0.65*)	23,000 (0.73)
Coarse silt	93,000 (0.18)	82,000 (0.04)
Medium silt	130,000 (0.05)	88,000 (0.16)
Fine silt	110,000 (0.05)	93,000 (0.11)
Clay	120,000 (0.00)	83,000 (0.16)

* Coefficient of variation = $\frac{\text{standard deviation taken over all sediments}}{\text{mean value}}$

of the sand. Also, the K_{oc}'s for sand were generally less than half those for finer fractions. This reduces the sorptive contribution of the sand in a composite sediment to that of a diluent of the fines for most applications. In addition, replicate determinations of K_p on a given sand fraction frequently differed by a factor of 2. Therefore, to estimate the K_{oc} of sand as 20% of the K_{oc} for the fines should not introduce any substantial error into the estimation of a composite K_p for most sediments. The required set of K_{oc}^i is now reduced to a determination of K_{oc} for sediment fines ($< 50\,\mu$m).

Sorption dependence on sorbate properties

Table 4 shows water solubilities taken from the literature, octanol/water distribution coefficients (K_{ow}), and K_{oc}'s for a series of polycyclic aromatics and chlorinated hydrocarbons. The compounds were chosen to span the range in water solubility from approximately 1 ppb to 1000 ppm. The K_{oc}'s reported are averages for isotherms run on the coarse silt fractions of the Doe Run and Hickory Hill sediments. Figure 5 shows K_{oc}'s plotted against both water solubilities and octanol/water distribution coefficients. The correlation coefficient (γ_{xy}) between K_{oc}'s and K_{ow}'s was 0.98 and between K_{oc}'s and water solubilities was -0.20. The K_{oc} correlation with K_{ow} is excellent; there is a rather poor linear correlation in K_{oc} relating to compound solubility.

Linear least-squares fitting of the K_{ow} and K_{oc} data gave the equation:

$$K_{oc} = 0.63\,K_{ow}\ (r^2 = 0.96). \quad (5)$$

Fitting to an equation that established a non-zero ordinate intercept gave comparable fits (based on r^2) for a broad range of intercept values, because of the lack of data in the 'low' K_{oc}–K_{ow} region. Therefore, the intercept was dropped in favor of the simpler equation (5).

Least squares fitting the log–log plots in Fig. 5 gave

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21\ (R^2 = 1.00) \quad (6)$$

and

$$\log K_{oc} = -0.54 \log S + 0.44\ (R^2 = 0.94), \quad (7)$$

where S is the water solubility expressed as mole fraction, and R^2 is the linear regression coefficient of determination. Equation (6) reduces to equation (5), indicative of the linear covariation of K_{oc} and K_{ow}. K_{oc} varies nonlinearly with S as described by equation (7).

These relationships associating sorption to octanol/water partitioning and solubility allow the K_{oc} for the 'fines' fraction of a sediment to be estimated from more easily determined and widely cataloged molecular parameters (Leo *et al.*, 1971). This K_{oc} estimate can be used in equation (4) to calculate a partition coefficient for a composite sediment.

Octanol/water partitioning provides a much better estimator for sediment–water partitioning than does solubility, which gives at best an order of magnitude estimate of K_{oc}. This derives from a combination of factors:

1. In a molecular sense, the partitioning of a compound between water and either sediment or octanol involves monomer distribution between two phases. On the other hand, saturated aqueous solutions involve the equilibration of primarily dissolved monomers with *crystalline* compounds. Thus, crystal energy contributions enter into water solubilities but do not affect the monomer-associated properties of K_{ow} and K_{oc}.

Table 4. Sorption dependence on sorbate properties

Compound	Water solubility Mole fraction × 10^9	ppb	K_{oc} × 10^{-3}	K_{ow} × 10^{-3}	$\frac{K_{oc}}{K_{ow}}$
Pyrene	12*	135	84	150	0.56
Methoxychlor	6.3†	120	80	120	0.67
Naphthalene	4460	31,700	1.3	2.3	0.57
2-Methylnaphthalene	3220	25,400	8.5	13	0.65
Anthracene	7.57	73	26	35	0.74
9-Methylanthracene	24.4	261	65	117	0.56
Phenanthrene	130	1290	23	37	0.62
Tetracene	0.037	0.5	650	800	0.81
Hexachlorobiphenyl	0.048‡	0.95	1200	2200	0.55
Benzene	410,000§	1,780,000	0.083	0.13	0.64

* The polycyclic hydrocarbon solubilities were taken from Mackay & Shiu (1977).
† From Zepp *et al.* (1976).
‡ Measured by Chiou *et al.* (1977) for 2,4,5,2',4',5'hexachlorobiphenyl.
§ From McAuliffe (1966).

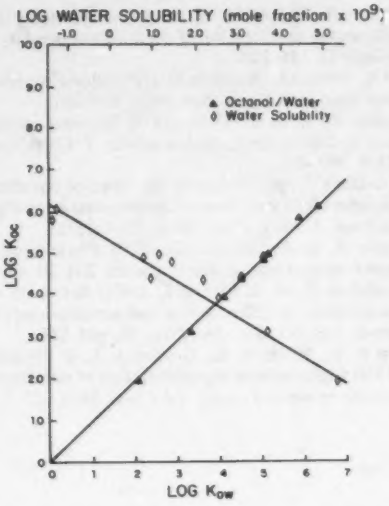

Fig. 5. Sorption K_{oc} as a function of compound water solubility and octanol/water distribution coefficients.

2. Both K_{ow}'s and K_{oc}'s listed in Table 4 are for systems wherein the aqueous solution concentrations of compound are considerably below the water solubility for the compound. As the water solubility is approached, K_{ow} shows a slight dependence on compound concentration, and the K_p (and thus K_{oc}) shows a very significant change with concentration. The reduced K_{oc} correlation with solubility could reflect the differences in 'water loading' in the respective systems.

3. The water solubilities are values from the literature, not run on the same compound samples as were the other data. Errors introduced in the absolute values of K_{ow} and K_{oc} as a result of impurities in the compounds will tend to cancel when the quantities are interrelated. Also, the solubilities were measured at various temperatures (22–25°C).

Octanol water partitioning

Literature K_{ow}'s for a given compound frequently vary over several orders of magnitude. This is especially true when the K_{ow}'s are 10^4 or greater. This variation is largely experimental in origin and stems primarily from the following sources:

1. Presence of impurities that are not analytically distinguished from the parent compound. Traces of more-water-soluble contaminants can substantially reduce the measured K_{ow}.

2. Compound loss from the water phase during phase separation and analysis. Hydrophobic organics tend to sorb or volatilize out of aqueous solutions during handling.

3. Contamination of water-phase sample with excess (beyond equilibrium value) octanol during the sampling process. Because of the magnitude of the K_{ow}, mass balance determination will often not reflect these errors in the water phase measurements.

In addition to these potentially large variations of experimental origin, smaller changes in K_{ow} were observed as a function of compound concentration. Not-all compounds were investigated in this respect, but the K_{ow}'s for the polycyclics in class 1 tended to increase (as much as 20%) as the aqueous concentration increased from half-saturation to saturation. The K_{ow}'s reported in Table 4 were measured at water concentrations of half-saturation or less (where no concentration dependence of K_{ow} was observed). The coefficient of variation for replicate determinations was generally less than 0.1 except in the case of hexachlorobiphenyl and tetracene, for which replicates varied as much as a factor of 2.

SUMMARY AND CONCLUSIONS

Sorption isotherms for all the hydrophobic compounds studied (water solubility from 500 ppt to 1800 ppm) were similar. They were linear over a broad range of aqueous phase compound concentrations. The linear partition coefficients (K_p) were relatively independent of sediment concentration and salt content in the suspensions. Mixtures of hydrophobic compounds sorbed independently through the linear portions of their respective isotherms. The K_p's for a given compound were directly related to organic carbon content for a given particle size isolate in different sediments. On an organic carbon basis (K_{oc}), the sand fraction was a considerably less effective sorbent (50–90% reduction in K_{oc}) than the fines fraction (sediment particles $< 50\,\mu m$). Differences in sorption within the silt and clay fractions were largely the result of differences in organic carbon content. The K_{oc}'s of the different hydrophobic compounds could be estimated from octanol/water distribution coefficients.

In conclusion, reasonable estimation (within a factor of 2) of the sorption behavior of hydrophobic pollutants can be made from a knowledge of the particle size distribution and associated organic carbon contents of the sediment and the octanol/water distribution coefficients of the pollutant. All of these sorbate–sorbent properties are either known or can be easily measured in the laboratory.

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